POLYMER-NANOPARTICLE-MODIFICATION OF BITUMEN USING STYRENE-BUTADIENE-STYRENE (SBS) TRIBLOCK COPOLYMER, CRUMB RUBBER (CR) AND FUMED NANOSILICA.

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By

Ajay Prasad Dhawale

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ABSTRACT

Bitumen is most commonly used as a binder in road pavement construction. Due to the harsh climate changes and heavier traffic loads, bitumen tends to undergo rutting and cracking which severely limits its service life and durability. Bitumen-based binders containing various proportions of styrene-butadiene-styrene (SBS) triblock copolymer, crumb rubber (CR) and fumed nanosilica have been synthesized. The modified binders have been studied for rheological properties, storage stability, nanoparticle dispersion, and thermal resistance. In addition, binder-sand composites have been prepared in a binder/sand weight ratio of 1:9 and have been tested for three-point flexural bend tests. Addition of nanosilica dramatically improves the rheological properties of bitumen with enhancements as great as 400% and the compatibility between bitumen and polymers is enhanced. In addition, CR-modified bitumen demonstrates a similar level of performance as SBS-modified bitumen, when both are used synergistically with nanosilica, which leads to beneficial environmental and economic impacts. Finally, the interfacial mechanisms between bitumen, polymers and nanosilica that are responsible for modification of bitumen using Fourier-Transform Infrared (FTIR) Spectroscopy and Dynamic Mechanical Analysis (DMA) were investigated and correlated with the performance of the materials.

Keywords: bitumen, styrene-butadiene-styrene (SBS), crumb rubber (CR), nanosilica, storage stability, interfacial mechanisms, recyclability

BIOGRAPHICAL SKETCH

Ajay Dhawale received his Master of Science degree from the Department of Materials Science and Engineering at Cornell University. He completed his Thesis in the Giannelis Research Group. He has previously completed his Bachelor of Technology degree from Institute of Chemical Technology, Mumbai in the field of Polymer Engineering and Technology. Ajay plans to use his theoretical and experimental knowledge that he gained from Cornell University to a more practical and industrial setting and would be working as a Module Engineer for Intel Corporation, Hillsboro, OR.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Bitumen is widely used in waterproofing membranes and as a binder for aggregates for pavements and is composed of a variety of fractions including saturates (S), aromatics (A), resins (R) and asphaltenes (A). Saturates, aromatics and resins are together known as maltenes. SARA fractions increase in molecular weight, polarity and aromaticity as S < A < R < As. Cong et al. [1] have defined saturates as straight or branched chain aliphatic hydrocarbon molecules (molecular weight (MW) of 300-20,000), aromatics (MW of 300-2000) as viscous liquids that act as a dispersion media for asphaltenes, resins (MW of 500-50,000) as polar molecules that act as a peptizing agent to reduce the asphaltene micelle size and enhance the fluidity of bitumen, and asphaltenes (MW of 1000-100,000) as highly polar complex materials. Properties of crude oil depend on the refinery process as well as the nature of the crude oil from which it was distilled [2]. An in-depth review of structure of bitumen can be obtained in the work of Leseur [3] who has defined the structure of bitumen as a colloidal dispersion of asphaltene fraction within maltenes where the asphaltenes are stabilized by the polar fraction of maltenes i.e. the resins.

Bitumen is used for pavements due to its viscoelastic properties. However, in response to harsh climate conditions, bitumen tends to undergo softening at higher temperatures in hotter regions and/or during summers as well as it becomes brittle at lower temperatures in colder regions and/or during winters. In addition to severe climate changes, increasing traffic loads and axle loadings add to the problems of poor service life of asphalt [4,5]. These distresses lead to a variety of failures in bitumen including fatigue cracking, rutting (permanent deformation), and low temperature thermal cracking. Thus, bitumen should be stiff enough at temperatures as high as 60°C for resisting the phenomenon of rutting and be flexible enough at very low temperatures to resist brittleness and consequent cracking. These properties are contradictory and hence, obtaining

a perfect balance of properties is tricky. Other factors influencing the performance of asphalt are its tendency to undergo oxidative and UV degradation, and its susceptibility to moisture damage. Hence, bitumen needs to be modified to enhance its service life and durability.

Modifying bitumen using polymers is a widely recognized strategy since polymers offer the advantages of higher stiffness at high temperatures (resistance to rutting), higher cracking resistance at low temperatures, moisture resistance, longer fatigue life, resistance to temperature sensitivity and stripping [6]. Some of the most commonly used polymers are styrene-butadiene-styrene (SBS) triblock copolymer, natural rubber (NR), ethylene vinyl acetate (EVA) block copolymers, atactic polypropylene [7], crumb rubber (CR) [8], low density polyethylene (LDPE) [9], high-density polyethylene (HDPE) [10], polyvinyl chloride [11] and, styrene-ethylene-butadiene-styrene (SEBS) copolymers [12]. However, SBS is widely accepted as the best performance enhancer for bitumen [13] and hence, it is most commonly used for bitumen modification. The styrene segments are considered as hard blocks which offer strength to bitumen whereas the soft blocks of butadiene offer flexibility to bitumen thereby improving both the high and low temperature characteristics of bitumen. SBS in presence of bitumen undergoes swelling due to the saturates and aromatic fraction of bitumen. The rigid blocks of polystyrene are dispersed in elastomeric blocks of polybutadiene [14]. SBS, typically used in a concentration range of 3-6 wt.% [15], offers the elastic properties of rubbers as well as the ease of processing of thermoplastics [12]. SBS forms the dispersed phase while bitumen forms the continuous phase. As the concentration of SBS is increased, a phase inversion is observed where SBS forms the continuous phase [16]. Disadvantages of SBS include high cost especially for this application as well as poor resistance to penetration and rutting at higher temperatures although low temperature flexibility is considerably improved. Besides SBS, another polymer modifier, which has gained

popularity in recent times is crumb rubber (CR). CR is commonly obtained by ambient temperature grinding or cryogenic grinding of waste car tires [17]. Advantages of using CR include utilization of a waste product like discarded tires, which further reduces the problem of waste disposal and reduces the occupancy of landfills by tires [18]. In addition to being a cheaper material, CR enhances the flexibility of the binder, reduces cracking, temperature susceptibility, traffic noise and maintenance costs and enhances skid resistance and durability of the pavement [19,20].

Kök and Çolak [13] have compared the effect of CR and SBS on mechanical and rheological properties of bitumen and have concluded that CR demonstrates a similar performance when used at a much higher concentration of 8 wt.% as compared to SBS, which is typically used at less than 5% concentration. Polymer modification of bitumen leads to binders with enhanced performance, however, polymer modification itself has some drawbacks. Besides high costs, low aging resistance, and high temperature sensitivity [16], the major drawback of polymers is that polymers and bitumen lack good compatibility. For instance, the compatibility of SBS and bitumen is poor and hence, the modified binder undergoes phase separation, which negatively affects its storage stability at higher temperatures [21]. Due to the poor interactions, polymers tend to undergo phase separation and hence, an asphaltene-rich phase and a polymer-rich phase are formed. Hence, the mixture does not remain homogenous and the properties are unevenly distributed. This leads to the weakening of high temperature rutting resistance and low-temperature fatigue and cracking resistance and the effect of polymer modification is lost [22]. Phase separation and the consequent poor storage stability become a major drawback when bitumen must be stored at high temperatures, for instance, during transportation or for it to be pumpable and workable [3]. This can also necessitate a specific design of storage tanks that need continuous agitation and hence, allow uniformity of temperature and homogeneity of material [23].

Different strategies have been employed to eliminate the drawbacks of polymer modification. These include making use of sulfur vulcanization, using antioxidants, using functionalization and reactive polymers, and using hydrophobic clay minerals [16]. Sulfur vulcanization is commonly believed to induce storage stability in polymer-modified bitumen by chemically crosslinking itself with the polymer and chemically coupling polymer and bitumen through either sulfide and/or polysulfide bonds [21]. However, with sulfur vulcanization, there are problems including its applicability to only unsaturated polymers, release of hydrogen sulfide, higher sensitivity to oxidative ageing and poor recycling options [21]. Antioxidants are known to scavenge free radicals while retarding the oxidative ageing. Although they retard oxidation and hence, prevent cracking and brittleness of bitumen, they are not much of help for storage stabilization. Besides, they are an expensive option. Clay minerals work optimally only when they are completely exfoliated by the polymer matrix. The use of nanoclays to improve the properties of polymers is already well documented [24, 25]. Jahromi and Khodaii [26] have investigated the effect of nanoclay on bitumen and have found that adding nanoclay leads to binders with higher stiffness, ageing resistance, lower penetration and ductility and higher softening point. SBS and hydrophobic MMT-modified bitumen was investigated by Zhu J. et al. [16] and Golestani et al. [27] which led to the observation of better rutting resistance, increased viscosity, and higher level of stiffness though the problem of storage stability persisted. Liu et al. [28] have investigated the effect of organo-modified montmorillonites on bitumen binders without the addition of any polymers and observed that nanoclays help improve the short-term aging resistance. However, the material was not storage stable in long-term aging tests. Pamplona et al. [29] used organically modified vermiculite and montmorillonite fillers and noticed that the binder containing 2.5% SBS and 2.5% nanoclays showed a similar improvement as the binder modified by 4.0% SBS, which

suggests that the nanoclays can act as substitutes for polymers. However, only the vermiculite based system showed improved storage stability. In addition, it was proved recently (Kosma et al., submitted) [31] that organomodified montmorillonite acts synergistically with the polymer additives SBS and CR, requiring less polymer and leads to a remarkable improvement of properties of bitumen both at ambient and elevated temperatures, and a stable system under storage conditions. However, usually clay remains as an intercalated structure and the exfoliation is not complete although Galooyak et al. [31] have successfully established an exfoliated structure of montmorillonite and have improved the physical properties like softening point, rheological properties like complex modulus and storage stability of SBS-modified bitumen and reduced penetration.

Beyond nanoclays, with the advent of nanotechnology, use of other nanofillers have shown some promising results in enhancing the performance of polymer-modified bitumen. Nanomaterials offer the advantages of high surface area and high aspect ratio. Nanofillers act as a compatibilizing agent between bitumen and polymer as well as a mechanical reinforcement for bitumen. A variety of nanofillers have been investigated for bitumen modification including nano-zinc oxide (ZnO), nano-calcium carbonate ($CaCO_3$), nano-Fe_2O_3, carbon nanotubes, etc. Zhu C. et al. [32] have compared the effect of nano-ZnO and organic expanded vermiculite on the rheological properties of bitumen before and after aging. Zhang et al. [33] have evaluated the rheological, morphological, and chemical properties of nano-ZnO, nano-TiO_2 and nano-$CaCO_3$ on SBS-containing bitumen.

Nanosilica has been used for drug delivery, medicinal applications, and cosmetics. However, nanosilica has relatively been unexplored for bitumen modification. Nanosilica offers multiple advantages of higher surface area, good dispersion, high chemical purity and excellent

stability [34], which makes it a very competitive filler for bitumen modification. Yusoff et al. [35] have investigated the effect of nanosilica on polymer-modified bitumen and have pointed out that nanosilica when used at 4 wt. % concentration leads to maximal improvement in resistance to moisture, oxidation, rutting and fatigue failure. Zhang et al. [36] have investigated the effect of a variety of nanofillers including nano-SiO_2, nano-TiO_2, and nano-ZnO and the effect of surface-modification of these fillers using silane coupling agent in improving the UV aging properties, storage stability and physical properties. Shafarbakhsh and Ani [5] have pointed out the effect of nano-SiO_2 and nano-TiO_2 on the physical properties, rheological properties and rutting and fatigue behavior of steel slag asphalt mixtures. Polydimethylsiloxane (PDMS)-modified nanosilica was used in this work. The major reason for using PDMS surface groups as opposed to other silicones and silanes was that PDMS has higher hydrophobicity compared to other shorter silicones/silanes due to its larger size and organic content. This higher level of hydrophobicity due to the organophilic modification on the silica surface enables nanosilica to be evenly distributed in a similarly hydrophobic medium like bitumen. In addition, it is proved further that the physical chain length of the surface grafted groups of nanosilica surface promote physical interactions with the polymer additives like SBS and CR. There could be counter-arguments about the choice of a silicone backbone for a modified silica surface as opposed to a carbon backbone, for instance, polystyrene. It should be noted that bitumen could be subjected to temperatures as high as 200°C during its processing and/or storage. At such high temperatures, surface groups containing a thermally stable backbone structure like Si-O-Si would be preferable in comparison to an organic backbone which is susceptible to thermal degradation at these temperatures although polystyrene might allow a higher level of hydrophobicity. Si-O-Si bond has higher bond energy as compared to C-C bonds and would be able to better withstand the thermal degradation.

The work in this thesis shows the effect of even small concentrations of nanosilica in improving the storage stability of SBS and/or CR-modified bitumen, rheological properties of pure bitumen, and mechanical properties of bitumen/aggregate mixtures. In addition, this work shows that CR demonstrates the same level of performance in modifying bitumen as SBS at the same loading when used synergistically with nanosilica. This establishes the fact that a cheaper and recycled material of CR can be effectively used to substitute an expensive and petroleum-based material (SBS) when used with nanosilica. Thus, this modification strategy can be very advantageous from an economic and environmental point of view. Although many investigations have revealed the beneficial impacts of using nanofillers, an in-depth investigation of chemical and physical interactions occurring within the systems is still unclear and is necessary for a deeper understanding of bitumen modification. This work has attempted to explicate the underlying mechanisms occurring at the interfaces between bitumen, polymers and nanosilica that cause the compatibilization of bitumen and polymers as well as improvements in rheological and mechanical properties.

2. EXPERIMENTAL

2.1. MATERIALS AND METHODS

2.1.1. Materials

Bitumen grade PG 64-22 (Suit-Kote Corporation), styrene-butadiene-styrene (SBS) triblock copolymers with 30 wt.% styrene (Sigma-Aldrich) and crumb rubber (CR) (30-mesh, Crumb Rubber Manufactures, CRM) were used as received. Aerosil®R202 fumed silica, referred to as nanosilica for simplicity in this thesis, (surface modified with polydimethylsiloxane (PDMS), SiO_2 content $\geq$ 99.8%, carbon content of 3.5-5%, average primary particle size of 14 nm and

specific surface area of 80-120 m^2/g) and Aerosil®R972 (surface modified with dimethyldichlorosilane (DDS), SiO_2 content ≥ 99.8%, carbon content of 0.5-1.2%, average primary particle size of 16 nm and specific surface area of 90-130 m^2/g) were obtained from Evonik Industries and were used as received. In addition, polydimethylsiloxane liquid (85409 Sigma-Aldrich, Silicone oil) and S5505 Sigma (unmodified fumed nanosilica), average primary particle size of 0.2-0.3 μm, specific surface area of 200 ± 25 m^2/g were obtained from Sigma-Aldrich. Concrete sand with particle size less than 0.84 mm (or 0.0331 inches) was used as received.

2.1.2. Sample Preparation

2.1.2.1. Binder Preparation

Samples were prepared using a VWR-14216-268 General Purpose Mixer at a temperature of 185°C with a total mixing time of 3 hours. Pure bitumen was heated to 185°C in a beaker and SBS and/or CR were gradually added and melt-mixed for an initial 1.5 hours. After 1.5 hours, nanosilica was added and the mixture was mixed for additional 1.5 hours. For comparison, the control sample of pure bitumen was subjected to same mechanical shearing, temperature and mixing time as the ones used for modified binders. SBS and CR were used in at three different loading levels of 0 wt.%, 1.5 wt.% and 3 wt.%. Nanosilica was used at a previously optimized constant loading of 3%. Based on this, Table-1 shows the codes of various binders and their respective descriptions.

System #	Description
1	Control Sample (Pure Bitumen treated at 185°C for 3 hours)
2	Bitumen – SBS 3 wt.%
3	Bitumen – SBS 3 wt.% - Nanosilica 3 wt.%
4	Bitumen – SBS 1.5 wt.% - CR 1.5 wt.%
5	Bitumen – SBS 1.5 wt.% - CR 1.5 wt.% - Nanosilica 3 wt.%
6	Bitumen – CR 3 wt.%
7	Bitumen – CR 3 wt.% - Nanosilica 3 wt.%

Table-1: Codes for modified and unmodified binder systems

2.1.2.2. Binder/sand composite preparation

Binder and concrete sand (uniform sized) (with a weight ratio 1:9) were mixed at 185°C for 2 hours until a homogeneous mixture was obtained and samples for testing were hot-pressed at 160°C for 15 min to form specimens (5 cm x 2 cm x 0.5 cm) for three-point bending test.

2.1.2.3. Polymer/nanosilica composite preparation

SBS/nanosilica composites were formed by feeding the mixture of SBS and nanosilica (0 to 10 wt. %) to a twin-screw micro-extruder. The mixture was melt-blended for 5 minutes at 195°C. The extruded material was further compression molded at 195°C to form specimens (6 cm x 1 cm x 0.3 cm) for dynamic mechanical analysis (DMA).

2.3. CHARACTERIZATION

2.3.1. Rheological measurements

Rheological measurements were carried out on an Anton Paar rheometer using a parallel plate geometry (25 mm diameter). The final measurement gap was adjusted to 1 mm before each measurement. Frequency sweep tests were carried out in the range of 0.1 rad/s to 100 rad/s in the linear viscoelastic region at 60°C and 0.05% strain. Strain sweep tests were carried out in the range of 0.01% to 100% at 60°C and 1 Hz frequency.

2.3.2. Transmission Electron Microscopy (TEM) imaging

Specimens for TEM imaging were obtained using microtoming ultrathin sections with a thickness of 50-100 nm at -20 to -30°C using a Leica Ultracut UC7/FC7 Cryo-ultramicrotome equipped with a DIATOME diamond knife. The samples were imaged using a FEI Tecnai G2 T12 Spirit TEM operating at an acceleration voltage of 120 kV.

2.3.3. Storage stability tests

High temperature storage tests were used to evaluate storage stability. Samples were poured into a Teflon tube (diameter: 2.5 cm, height: 14 cm) and vertically placed in an air-circulating oven at 163°C for 48 h. Subsequently, the tube was removed from the oven and stored in a refrigerator at 25°C. Once cooled, the tube was cut into three parts of equal length; the middle part was discarded and the remaining two parts were collected for rheological observations

2.3.4. Mechanical testing

Three-point bend flexural tests were carried out on an Instron (5569) instrument . A strain rate of 2 mm/min was used. A total of four such specimens were tested for a given binder and the results were averaged to minimize experimental error.

2.3.5. Thermogravimetric Analysis (TGA)

TA Instruments TGA Q500 was used for TGA. 5-10 mg of sample were placed in an aluminum crucible which itself was placed in a platinum pan and the temperature was ramped with a heating rate of 10°C/min and final temperature of 500°C in the presence of nitrogen with a flow rate of 40 mL/min for sample. Weight loss was calculated as a function of temperature.

2.3.6. Fourier-Transform Infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra of pure and modified bitumen samples as well as individual components (SBS, CR and nanosilica) were obtained between 4000 cm^{-1} and 500 cm^{-1} with a Thermo Fisher Scientific NICOLET-iZ10 FTIR spectrometer.

2.3.7. Dynamic Mechanical Analysis (DMA)

Temperature sweep tests using TA Instruments DMA Q800 Dynamic Mechanical Thermal Analysis (DMTA) were carried out between temperatures of -120°C to 130°C with a scanning rate of 5°C/min at 0.2% strain and 1 Hz frequency in the presence of nitrogen gas.

3. RESULTS AND DISCUSSIONS

3.1. Rheological Properties

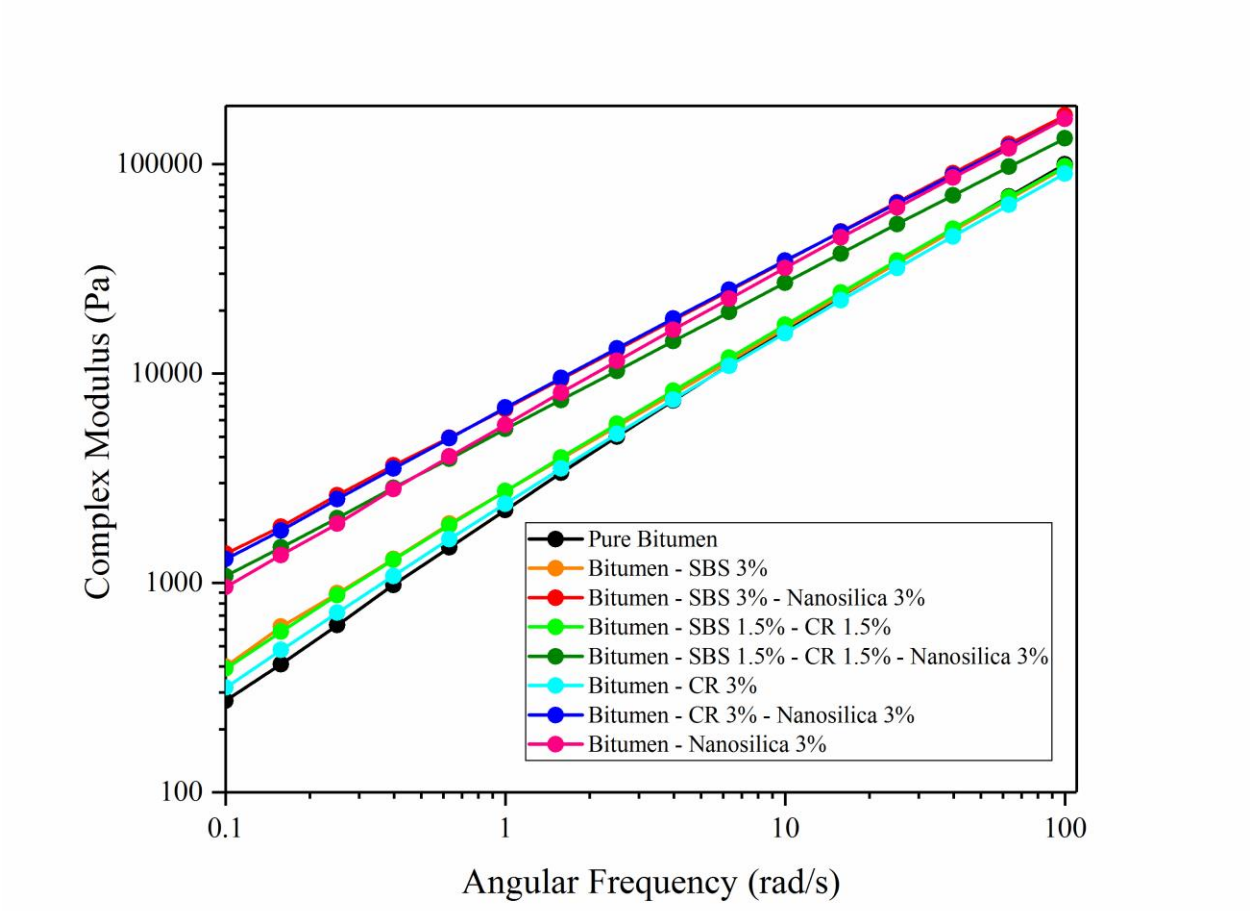


Figure-1: Complex moduli response to frequency sweep for modified and unmodified bitumen

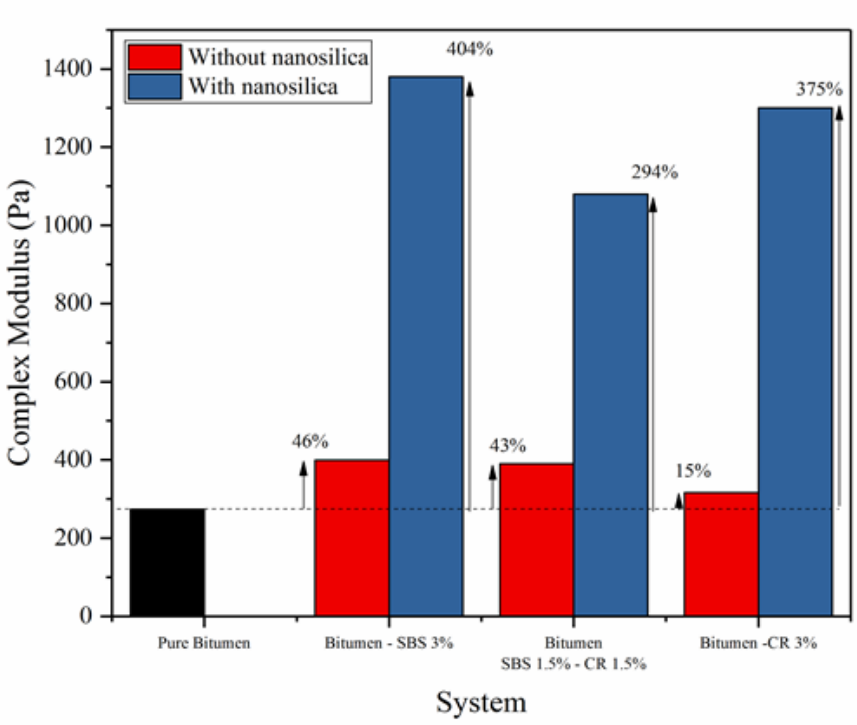
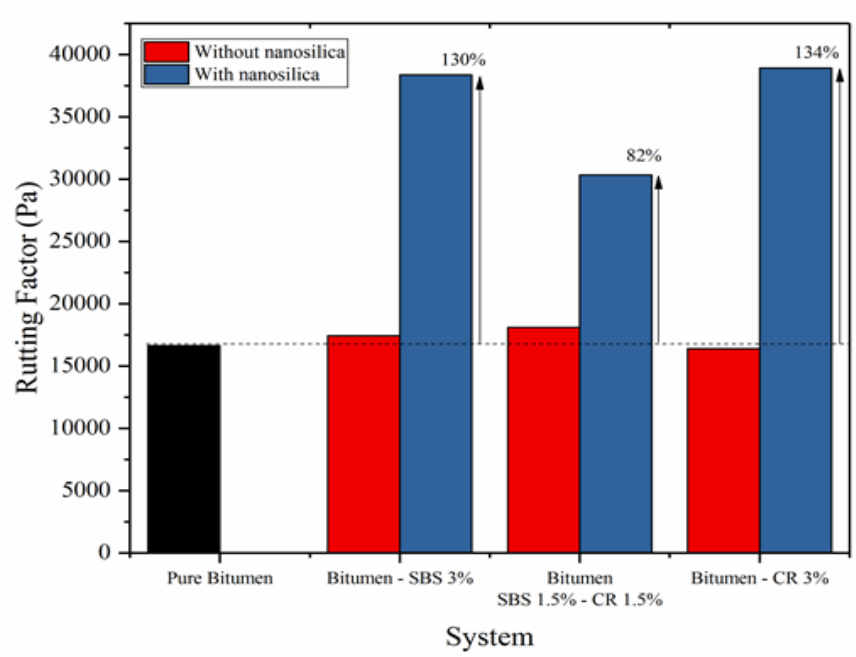


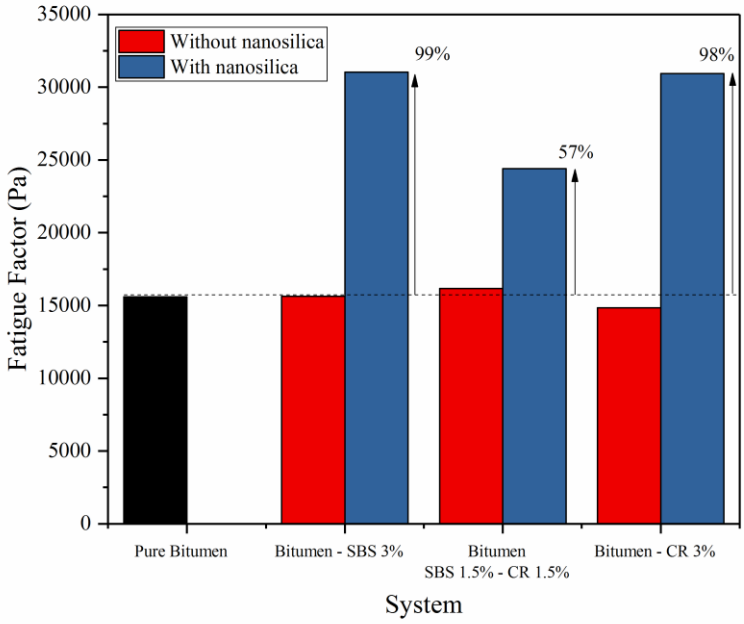
Figure-2: Comparison of complex moduli at 0.1 rad/s and 60°C

Complex modulus is defined as a ratio of maximum shear stress to maximum strain and is used as a measure of total resistance to deformation when the material is subjected to shear loading [37]. It can be seen from Figure-1 and Figure-2 that addition of SBS and/or CR leads to binders with enhanced complex moduli. The increase is even higher for samples containing nanosilica. Although CR-modified bitumen demonstrates a lower complex modulus compared to SBS-modified bitumen, addition of nanosilica seems to make them similar in terms of complex moduli. Thus, it can be assumed that nanosilica and polymers act synergistically which leads to such superior enhancements in the complex moduli of modified binders. This could lead to an advantageous development from economic and environmental point of view. Combining SBS and CR in a weight ratio of 1.5%:1.5% leads to improvements in binder, however, to a lesser extent as the other nanosilica-containing binders. This is probably due to the presence of a multiple (four) component system (bitumen, SBS, CR, and nanosilica), which leads to poor compatibility and

interfacial interactions between fillers, polymer modifiers and bitumen due to the differences in their densities, solubility parameters and interaction levels. TEM images (Figure-5) confirm these results by indicating smoother morphologies for SBS/nanosilica-modified bitumen and CR/nanosilica-modified bitumen as compared to SBS/CR/nanosilica-modified bitumen where the phenomena of uneven distribution of nanosilica can be seen. Although nanosilica-modified bitumen in the absence of polymers demonstrates similar performance in terms of complex modulus, maximal improvement was observed when polymers were used in conjunction with nanosilica to modify bitumen. Hence, polymers were retained in the systems for further experiments and to utilize their low temperature properties like flexibility.



(a)



(b)

Figure-3: Comparison of (a) rutting factor and (b) fatigue factor of binders at 60°C and 10 rad/s

Based on these rheological measurements, the rutting factor ($G^*/\sin\delta$) was also calculated (Figure-3 (a)). Rutting factor is a measure of resistance to rutting or permanent deformation of binder as it considers the complex moduli of the binders as well as the loss angle (δ). The latter is the phase lag between stress and strain. Loss angle (or phase angle) describes the relative proportions of recoverable and unrecoverable deformations of binders. To simulate real traffic load conditions at 75-90 km/h, rutting factor was calculated at 10 rad/s [38]. Like complex moduli, it can be noted that polymer modifiers do not enhance the rutting factor of binders significantly when used by themselves. However, when these polymer modifiers are used synergistically with nanosilica, the rutting factor is enhanced to about 130% for SBS system and 134% for CR system. As seen before with the complex modulus, the improvement is only 82% in case of SBS/CR

system. Figure-3 (b) shows the fatigue factor (G*.sinδ) at 10 rad/s. As per Strategic Highway Research Program (SHRP) [39], fatigue factor can be used to understand fatigue properties of the material. Typically, higher value of fatigue factor implies higher value of sinδ. sinδ is proportional to δ which itself is proportional to the ratio of loss modulus to storage modulus. Hence, as fatigue factor increases loss modulus also increases and the shearing energy dissipates quicker under load and thus the fatigue resistance of binder decreases [40]. Figure-3 (b) shows that nanosilica does not necessarily improve the binder from the point of view of fatigue resistance. Realistically, it is very difficult to obtain a binder that possesses equally good rutting and fatigue resistance as these properties are contradictory to each other. However, binders are synthesized with the need of geographical locations. For instance, a higher level of rutting resistance is preferred in a place like Arizona that has higher temperatures and hence, low temperature fatigue resistance can be neglected. Similarly, low temperature fatigue and cracking resistance becomes crucial in places like Minnesota where cold temperatures are prevalent and hence, high temperature rutting resistance can be compromised. It is unlikely to have such great climate changes in a given place. Hence, the binder properties can be optimized by including higher loadings of polymers and rubbers to improve low temperature properties in colder regions whereas fillers like nanosilica which increase viscosity can be used more for regions with higher temperatures.

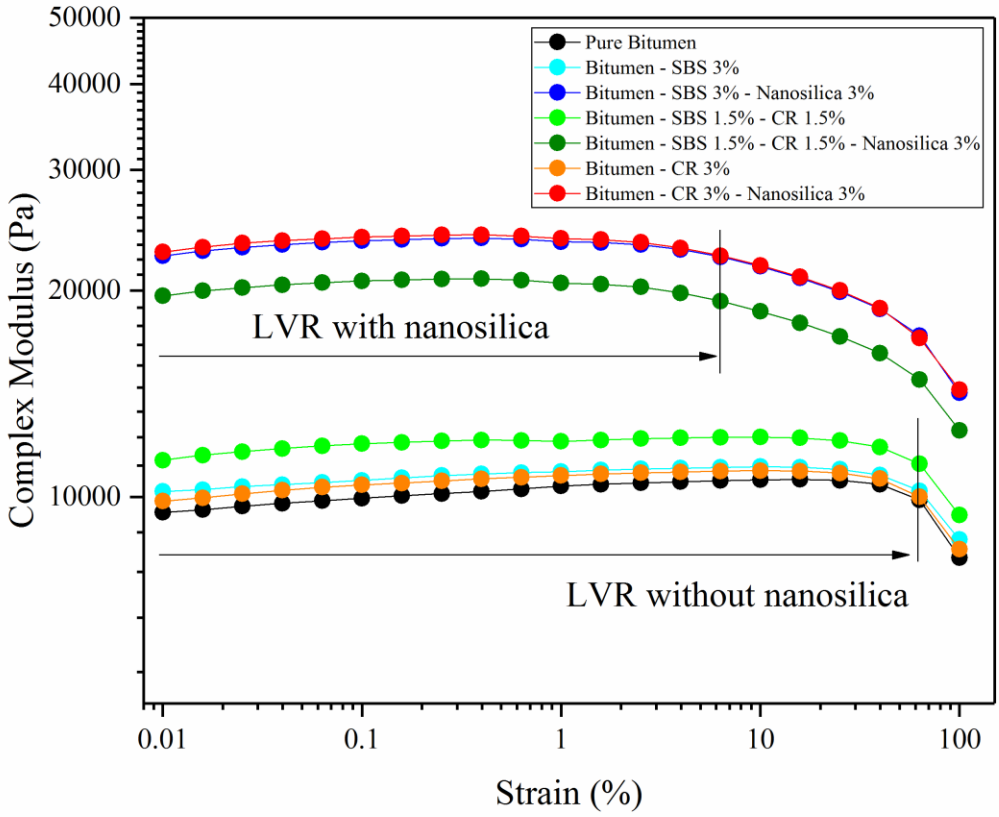
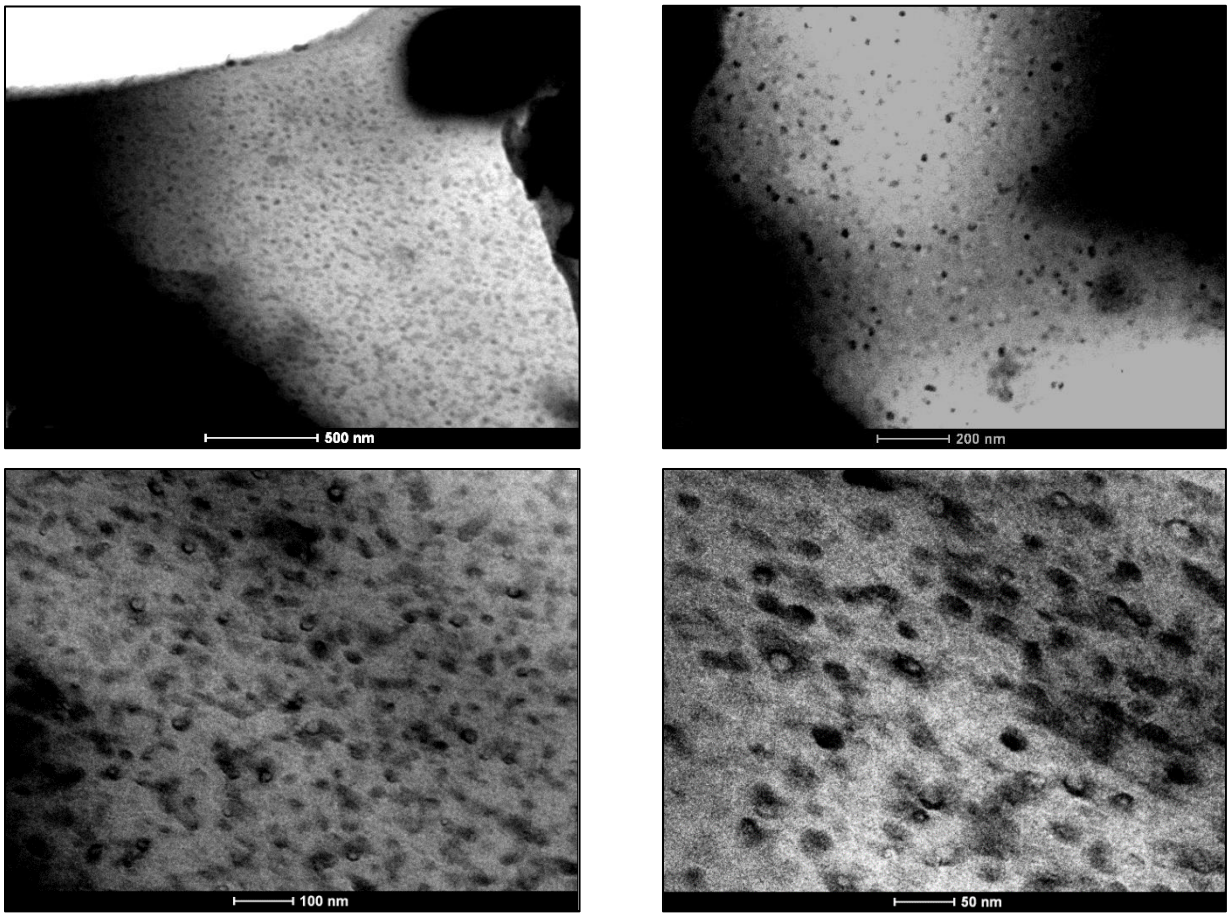


Figure 4: Complex modulus response to strain sweep for modified and unmodified systems.

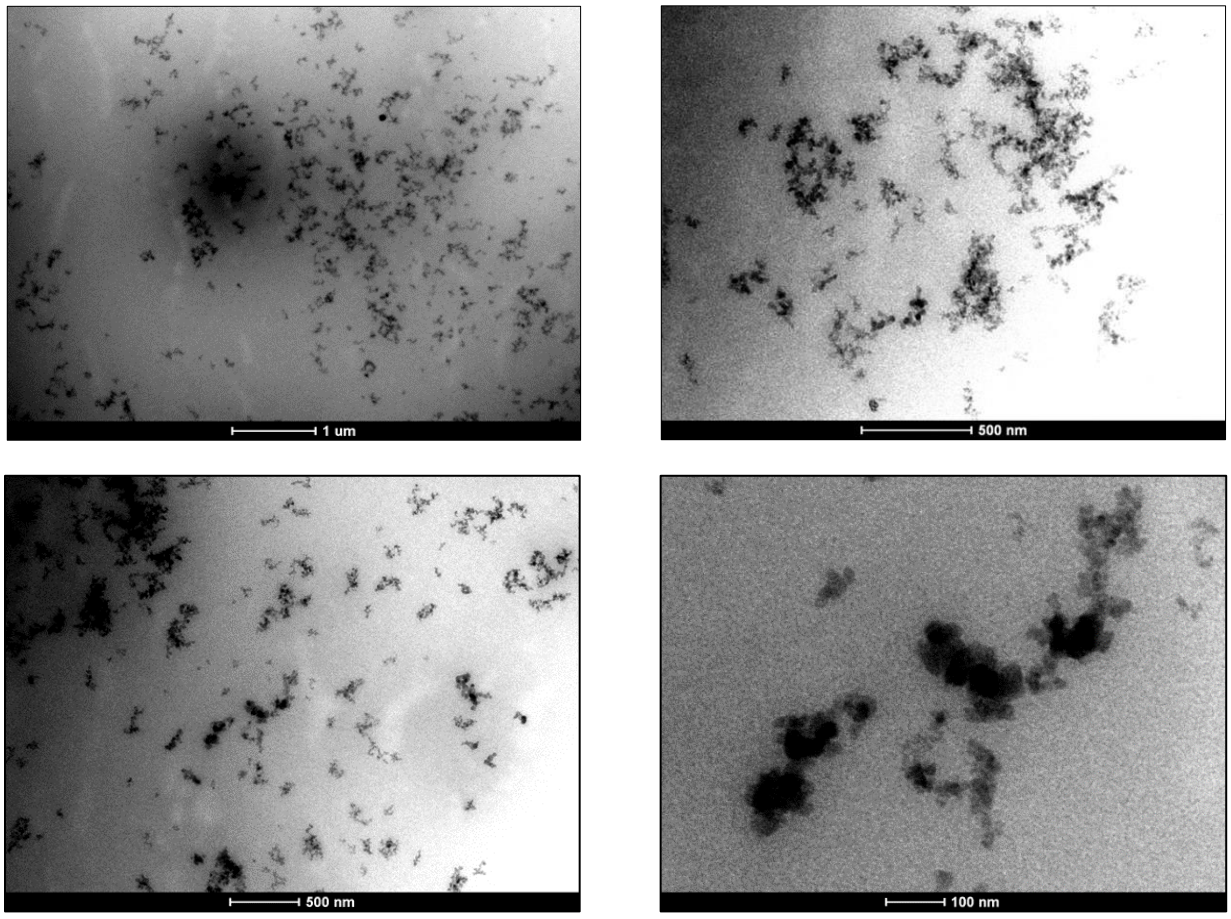
Strain sweep tests followed the same trend as the one observed with frequency sweep. According to Strategic Highway Research Program [39], linear region is defined as the range of strain values where the complex modulus is at least 95% of its zero-strain value. This is the region where complex modulus of the material is independent of strain applied on it. As seen in the Figure-4, pure bitumen exhibits the maximum linear viscoelastic region (LVR). It can also be seen that polymer modifiers of SBS and CR do not affect this LVR. However, as expected, the LVR is reduced after the addition of nanosilica due to increased stiffness and viscosity and reduced flexibility. Thus, nanosilica helps to stiffen the binder and simultaneously reduce the excessive

flexibility. This is not necessarily a disadvantage as excessive flexibility is undesirable as it is one of the primary reasons for the pavements' rutting phenomena.

3.2. Transmission Electron Microscopy (TEM) Imaging



(a)



(b)

Figure-5: TEM images for (a) Bitumen – SBS 3 wt.% - Nanosilica 3 wt.%

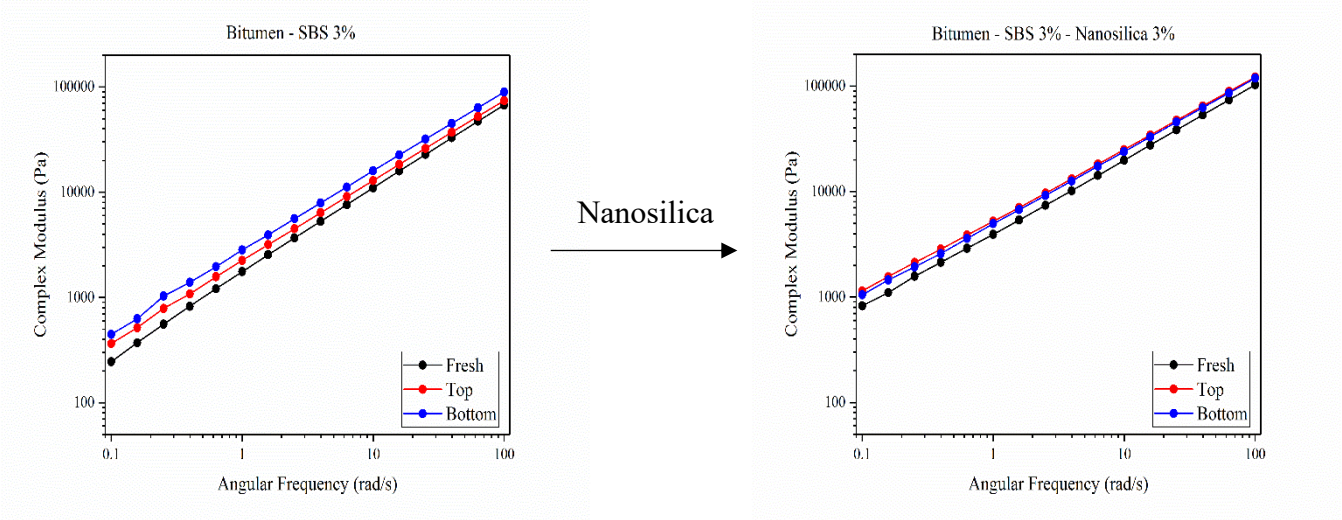
(b) Bitumen – SBS 1.5 wt.% - CR 1.5 wt.% - Nanosilica 3 wt.%

Additional microstructure information is provided by TEM imaging. To improve contrast the samples were stained with OsO_4. The complexity of bitumen chemistry lies in the fact that many different chemicals are present. As an overall descriptor, the chemical nature of the crude oil is generally described as paraffinic, naphthenic or aromatic, if a majority of saturated, cyclic or aromatic molecules, respectively, are present [41]. In general, osmium tetroxide reacts with

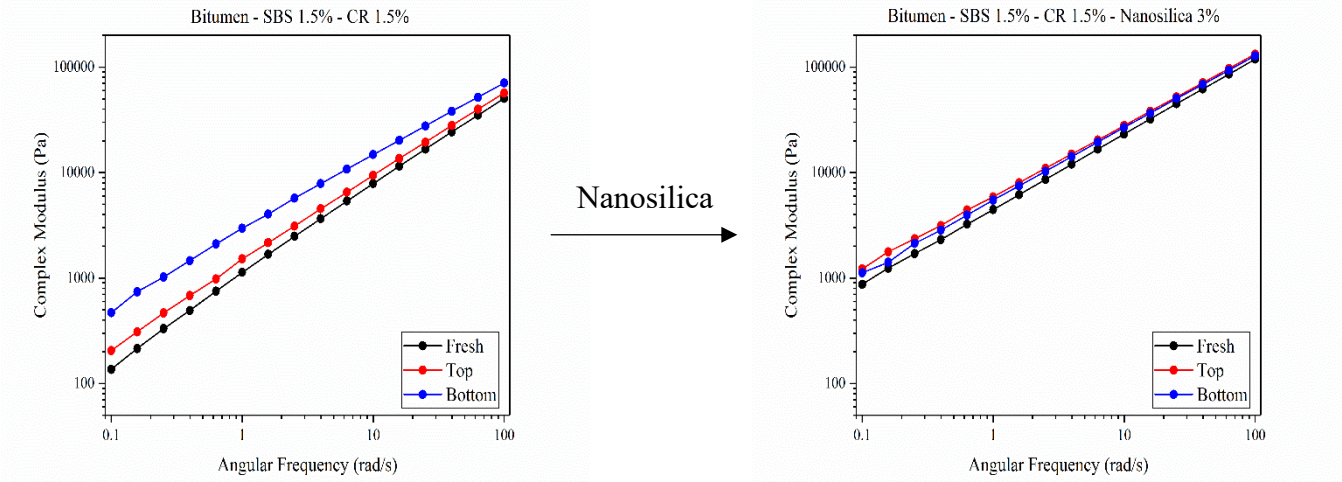
double-bonds. It reacts readily with ethylenic double bonds and more slowly with certain aromatic "double" bonds, to form organo-osmium compounds. The addition to these aromatic bonds takes place much more slowly compared to ethylenic bonds and to be more precise only the most reactive react. For instance, while benzene does not react under usual conditions, one bond is usually attacked in more reactive polycyclic compounds, as is the case with phenanthrene [42, 43].

Figure-5 shows some representative images for dispersion of silica in bitumen binders. It can be seen from Figure-5 (a) that nanosilica has a uniform dispersion in the SBS system with a particle size around 20 nm. However, it can be seen from Figure-5 (b) that the dispersion of nanosilica is not uniform in the case of SBS/CR system probably due to different levels of affinities of nanosilica towards SBS and CR. It can be concluded that the relatively lower mechanical properties in case of the SBS/CR system mainly result due to this phenomenon of uneven distribution of nanosilica.

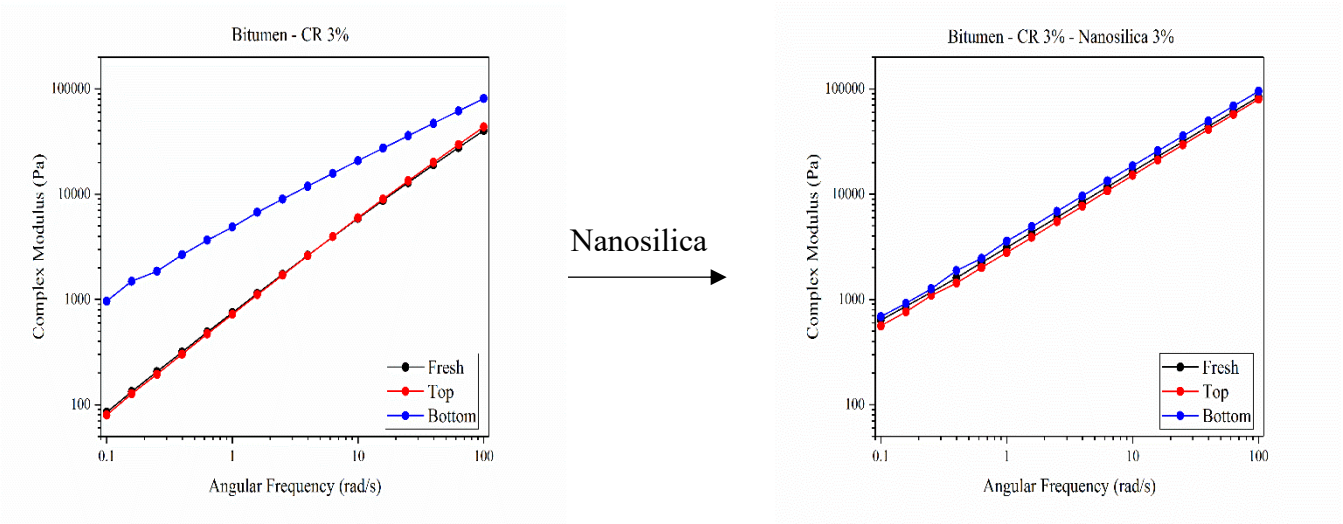
3.3. Storage Stability



(a) Bitumen – SBS 3% system



(b) Bitumen – SBS 1.5% - CR 1.5% system



(c) Bitumen – CR 3% system

Figure-6: Effect of nanosilica on storage stability of (a) Bitumen – SBS 3% system

(b) Bitumen – SBS 1.5% - CR 1.5% system and (c) Bitumen – CR 3% system

Storage stability was evaluated using the ASTM D5892-00 standard. In this test, we compare the complex modulus of the top and bottom parts of an aged sample using rheological measurements. Any settling will undoubtedly lead to a change in the modulus of the different parts. It can be seen from Figure-6 (a) that in absence of nanosilica, SBS and bitumen tend to undergo a phase separation. The main reasons for the phase separation is the difference between densities and solubility parameters of SBS and asphalt [31]. Similar, results were obtained in case of CR modified-bitumen, (Figure-6 (c)) where CR particles tend to settle down at the bottom of the tube and hence binder from the bottom section demonstrates a higher modulus than that of the top section. However, when nanosilica is added, it can be noticed that the frequency sweep plots of the top and bottom sections for all the three systems perfectly overlap (Figure-6(a-c)). Similar rheological measurements of samples from top and bottom sections mean that the composition of the sample throughout the tube is uniform. A certain level of drop in the frequency sweep plots

was observed relative to original measurements in Figure-1 due to the scaling up of batch, which caused inadequate heating of binder and hence, resulted in a lower level of stiffness. Besides the stiffening effect of the binder due to addition of nanosilica (observed through change in slope in Figure-6) which hinders the mobility of polymer additives, it can also be said that nanosilica acts at the interface of polymers and bitumen and thereby compatibilizes the polymers with the bitumen matrix. Similar experiments were done by Zhang et al. [33] where they have compatibilized SBS and bitumen using nanofillers like nano-TiO_2, nano-$CaCO_3$ and nano-ZnO. Zhang et al. [33] concluded that the morphology of polymer-modified bitumen is altered due to the presence of nanofillers because of their high surface area and energies. Nanofillers act to reduce the interfacial tension between the polymers and bitumen due to their strong tendency to bind with both the bitumen as well as polymer modifiers; the resultant interfacial structure between nanofiller and polymer and nanofiller and bitumen hinders the movement of polymers and leads to an increase the mechanical properties [33]. Alhamali et al. [44] have investigated the effect of nanosilica on polymer modified-bitumen and have attributed the nanosilica induced storage stability to physical and perhaps even some chemical interactions between polymers, fillers and bitumen. As seen from Figure-6 (c), CR seems to have a strong tendency to settle as seen from the difference in the complex moduli of samples from top and bottom parts of the tube. On the other hand, SBS-modified bitumen seems to have a lesser tendency to phase separate. Isacsson and Lu [45] have investigated a variety of polymers including styrene-ethylene-butylene-styrene (SEBS) copolymers for bitumen modification and have claimed that systems with low polymer concentrations, for example, SEBS (3 wt.%)-modified binder are storage stable, like SBS 3% in the present case.

Type of system	Separation Index log (G*asphaltene-rich phase/G*polymer-rich phase) (0.1 rad/s, | 0.05% strain | 60°C)	
	Without nanosilica	With nanosilica
Bitumen - SBS 3%	-0.09	0.04
Bitumen - CR 3%	-1.08	-0.09
Bitumen - SBS 1.5% - CR 1.5%	-0.36	0.04

Table-2: Separation index for modified binders

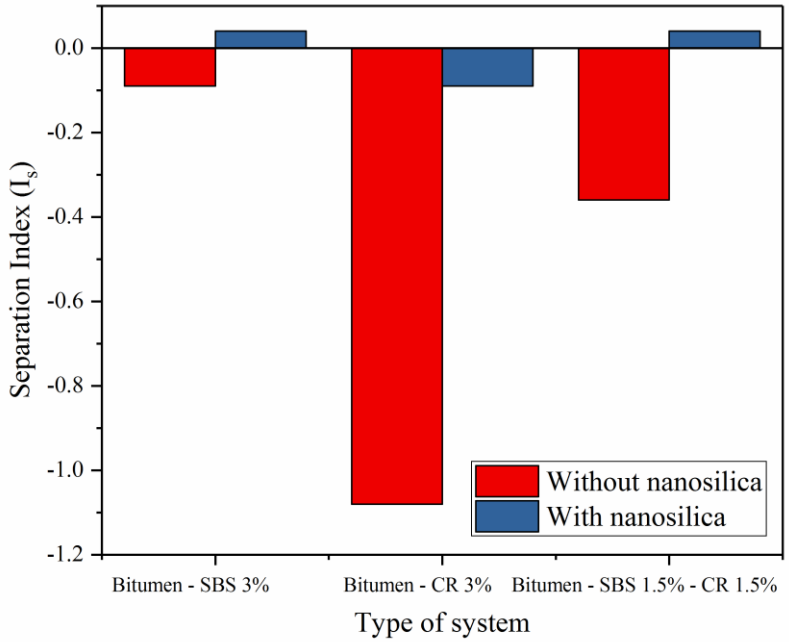


Figure 7: Effect of nanosilica on separation index of different bitumen systems

Due to settling of polymers like CR, the bottom part of the tube becomes the polymer-rich phase whereas the top-part remains as an asphaltene-rich phase. Based on these measurements, the separation index (I_s) is calculated as the logarithm of the ratio of complex modulus of asphaltene-rich phase (top part of the tube) to polymer-rich phase (bottom part of the tube) [45]. Table-2 shows the I_s values at 0.1 rad/s at 60°C. In the absence of nanosilica, the negative values of separation index are indicative of phase separation and poor compatibility of polymers and bitumen. However, in case of nanosilica-modified binders, due to the compatibilizing effect of nanosilica, these values approach zero (Figure-7). A separation index value of zero is ideal as it is essentially a characteristic of better compatibility between polymers and bitumen, uniformity of sample composition and minimum phase separation.

3.4. Mechanical Properties – Three-point bend flexural tests

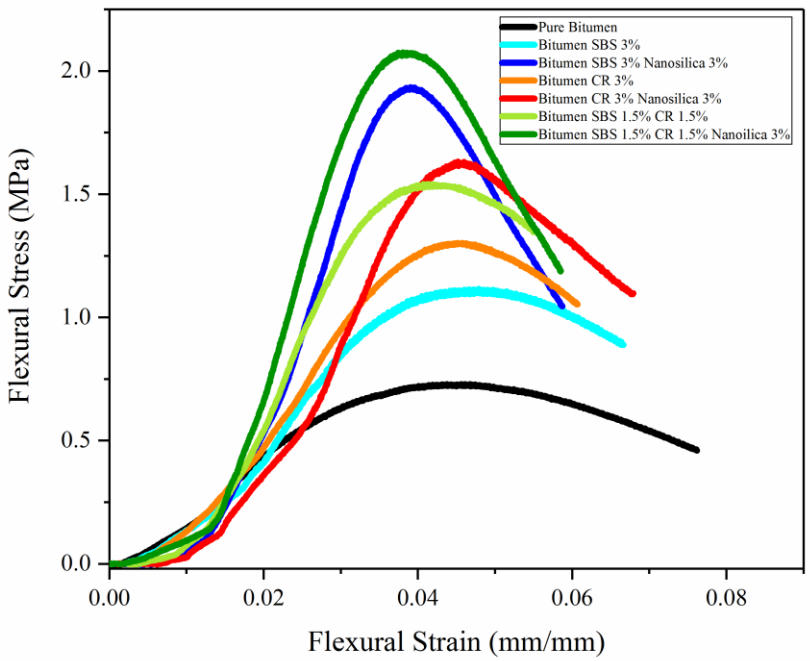
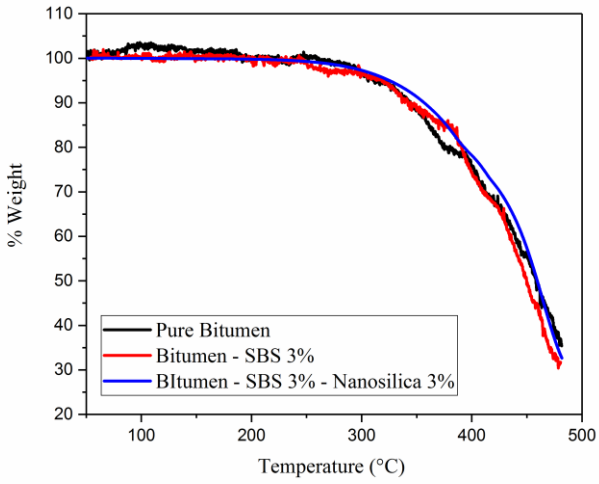


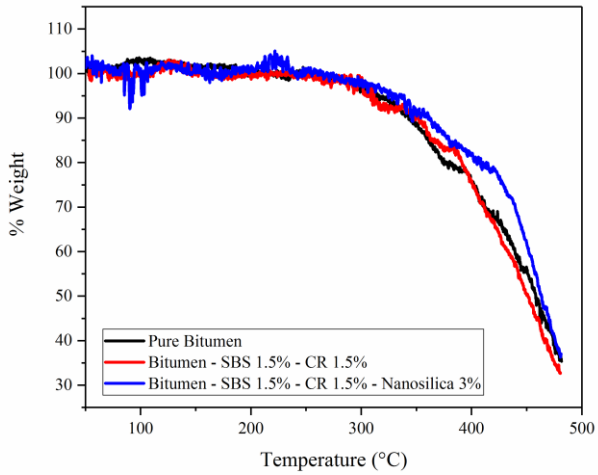
Figure-8: Mechanical properties of bitumen binder/sand composites

It is clear from the rheological measurements that binders modified with SBS and CR when used along with nanosilica lead to the formation of binders with enhanced rheological properties as compared to the control sample. To investigate the performance of the modified binders when used with aggregate, we prepared mixtures of binders and concrete sand (particle size less than 0.84 mm) in a 1:9 weight ratio and the mixtures were compression-molded at 150°C for 15 minutes to form specimens (5 cm x 2 cm x 0.5 cm) for three-point bend tests. In agreement with the rheological observations, we can observe from Figure-8 that the modified binders/sand composites demonstrate a higher strength as compared to unmodified binder/sand composites. Polymer modified bitumen/sand composites show improvement in the strength relative to pure bitumen/sand composites. The improvement is even higher for polymer-nanosilica-modified bitumen/sand composites. The strain at ultimate strength (maximum in curve) shifted towards somewhat lower values upon the addition of nanosilica, which was due to the stiffer behavior of nanosilica containing binders.

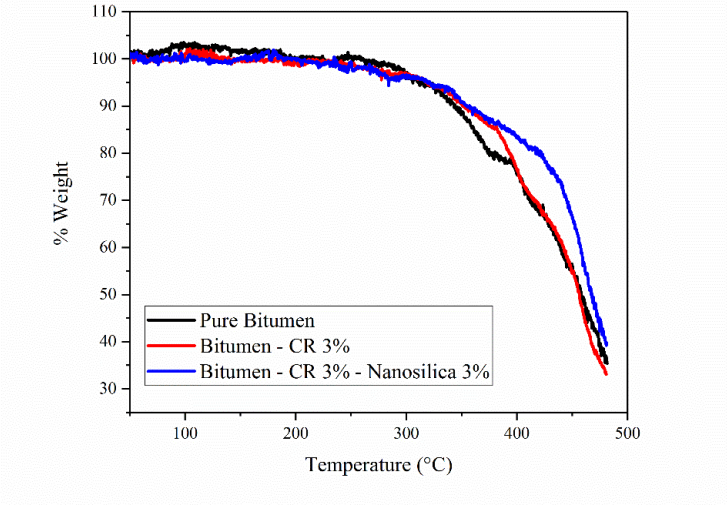
3.5. Thermogravimetric Analysis (TGA)



(a)



(b)



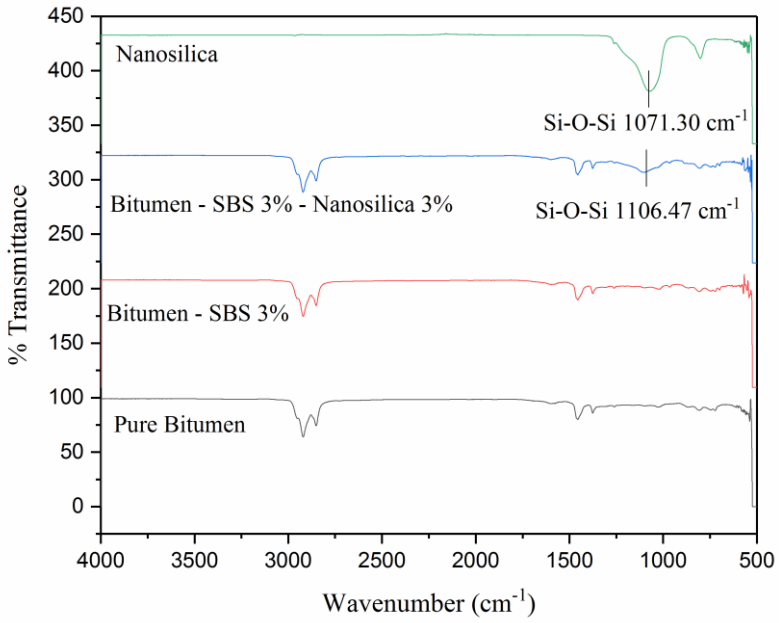
(c)

Figure-9: TG curves for (a) SBS 3% (b) SBS 1.5% - CR 1.5% and (c) CR 3% systems

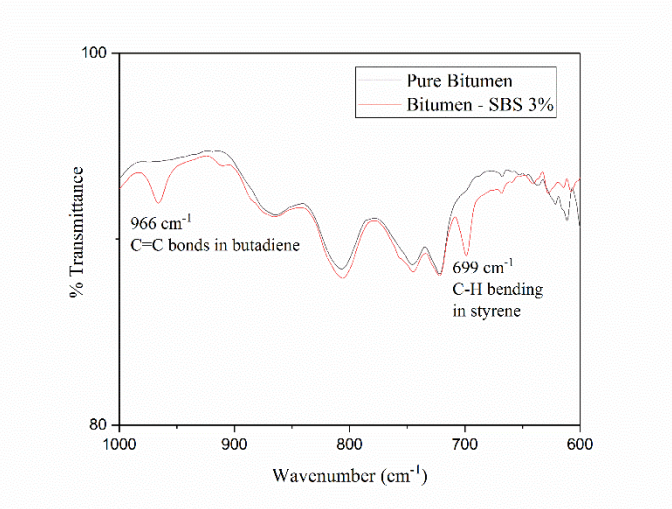
Studying thermal characteristics of bitumen is essential to estimate the high temperature stability. TGA is a quick and effective technique to understand the thermal characteristics of bitumen and bitumen based systems. Thermal degradation is undesirable since it makes bitumen

brittle and leads to cracking. Thermal degradation of bitumen is broadly classified into three regions. The first weight loss is in the range of 220-370°C and is mainly related to volatization of light components like non-polar aromatic hydrocarbons and saturated hydrocarbons in the bitumen. The second stage of weight loss is around 380-500°C and is due to the decomposition of asphaltenes and resins [46]. It can be seen from the above thermogravimetric (TG) curves (Figure 9(a-c)) that weight fraction of pure bitumen starts to drop at lower temperatures than those for the nanosilica-modified samples. It can also be noted that the plots of pure bitumen show a steeper slope at higher temperatures, which is indicative of rapid mass loss. However, in the presence of nanosilica, the slope is less steep and the degradation takes place gradually. In addition, at a given temperature (say 425°C), the nanosilica-containing samples demonstrate a higher level of weight fraction that was not decomposed as compared to the control sample. These observations indicate that the resistance to thermal degradation is improved by the addition of nanosilica. It can also be noted that the temperatures for the onset of degradation are slight higher for systems containing CR than the systems with only SBS. This is probably due to the presence of other additives like carbon black, silica and steel that are inherently present in CR as well as due to the crosslinked structure of CR, which is more temperature resistant than linear SBS. Since the temperature scale is analogous to time scale, it can be said that the kinetics of thermal degradation are slowed down and the thermal degradation process is retarded. A final stage of weight loss above 550°C (not shown here) can be expected which is mostly related to decomposition of asphaltenes. We can conclude that the addition of polymers and nanosilica leads to a more stable material.

3.6. Fourier-Transform Infrared (FTIR) spectroscopy

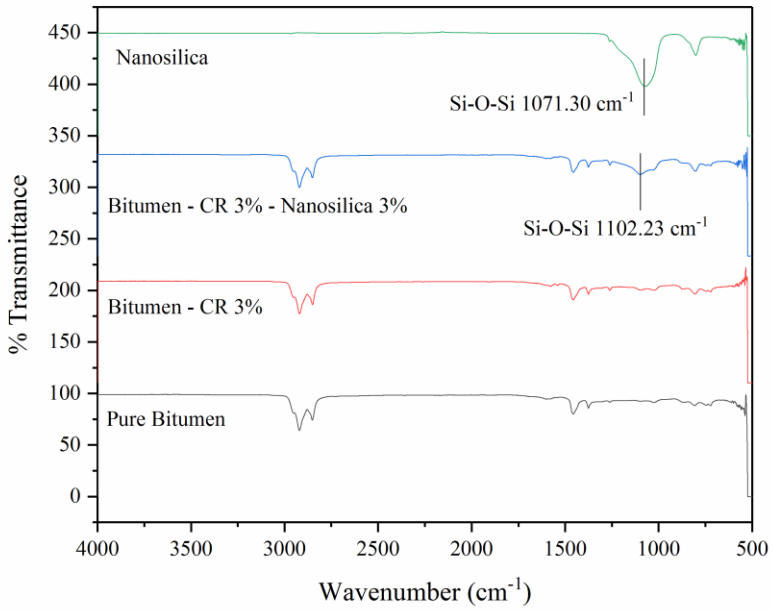


(i)

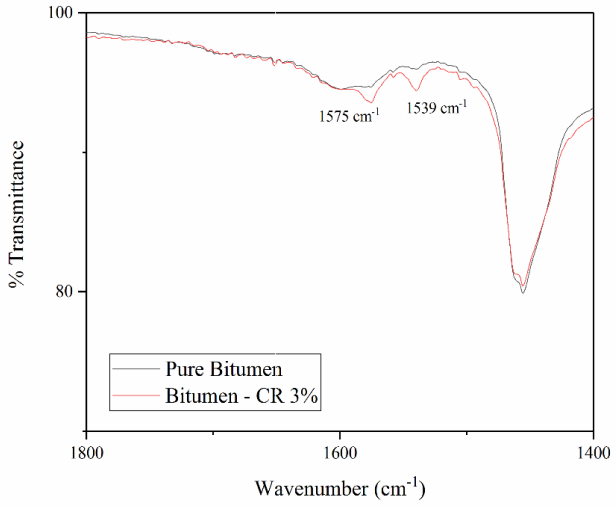


(ii)

(a)

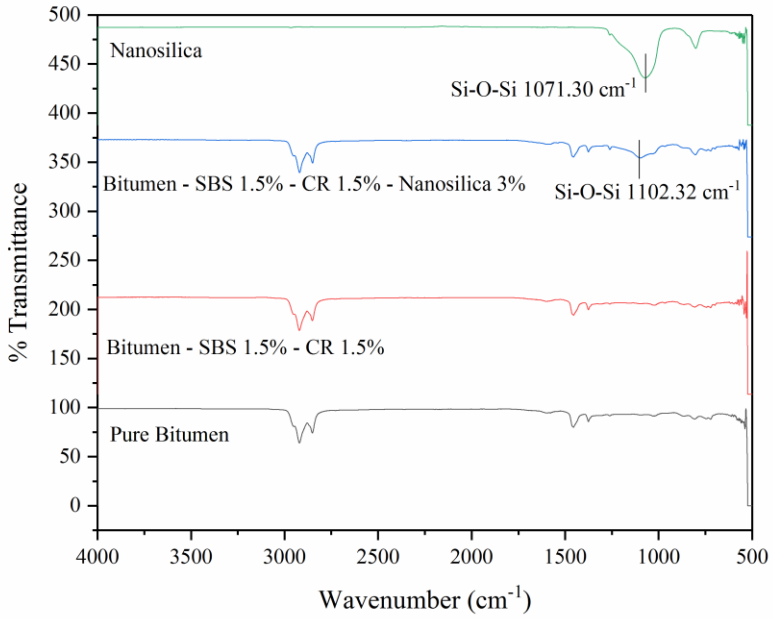

Nanosilica
Si-O-Si 1071.30 cm-1
Bitumen - CR 3% - Nanosilica 3%
Si-O-Si 1102.23 cm-1
Bitumen - CR 3%
Pure Bitumen
% Transmittance
Wavenumber (cm-1)

(i)

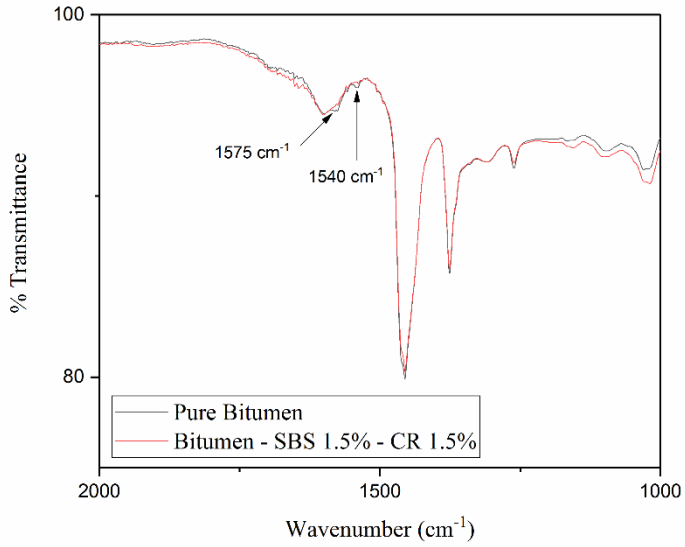

1575 cm-1
1539 cm-1
Pure Bitumen
Bitumen - CR 3%
% Transmittance
Wavenumber (cm-1)

(ii)

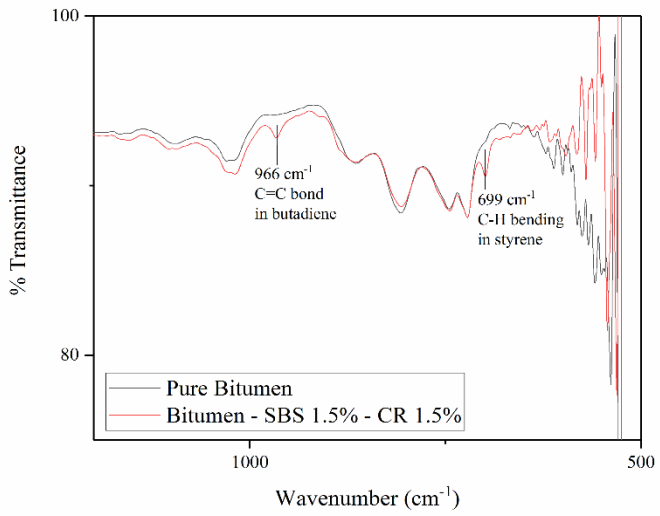
(b)


Nanosilica
Si-O-Si 1071.30 cm-1
Bitumen - SBS 1.5% - CR 1.5% - Nanosilica 3%
Si-O-Si 1102.32 cm-1
Bitumen - SBS 1.5% - CR 1.5%
Pure Bitumen
% Transmittance
Wavenumber (cm-1)

(i)

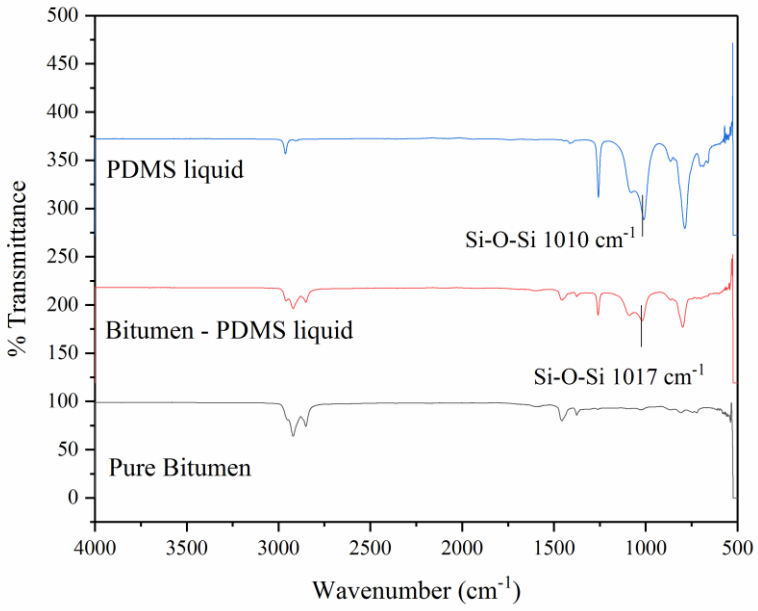

1575 cm-1
1540 cm-1
Pure Bitumen
Bitumen - SBS 1.5% - CR 1.5%
% Transmittance
Wavenumber (cm-1)

(ii)

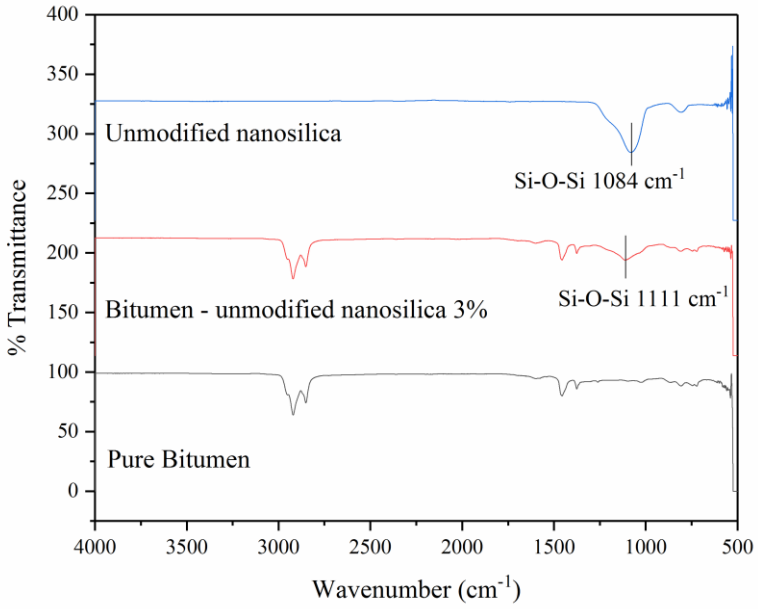

100
80
% Transmittance
966 cm-1
C=C bond
in butadiene
699 cm-1
C-H bending
in styrene
Pure Bitumen
Bitumen - SBS 1.5% - CR 1.5%
1000
500
Wavenumber (cm-1)

(iii)

(c)


500
450
400
350
300
250
200
150
100
50
0
% Transmittance
PDMS liquid
Si-O-Si 1010 cm-1
Bitumen - PDMS liquid
Si-O-Si 1017 cm-1
Pure Bitumen
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

(i)



(ii)

Figure-10: FTIR spectra for systems containing (a) SBS 3 wt.% (b) CR 3 wt.% and

(c) SBS 1.5 wt.% - CR 1.5 wt.% (d) PDMS and unmodified nanosilica modified bitumen

In the case of control sample of pure bitumen (Figure-10 (a-c)), strong peaks at 2920 cm^{-1} and 2851 cm^{-1} are observed which are a characteristic of stretching vibrations of C-H in aliphatic groups [47]. The peak at 1598.83 cm^{-1} is attributed to the stretching of C=C vibration in aromatic groups [7]. As stated by Nciri et al. [7], the peak at 1457 cm^{-1} is due to the asymmetric deformation of C-H in CH_2 and CH_3 while the peak at 1376 cm^{-1} is due to the symmetric deformation of C-H in CH_3. Th peak at 1700 cm^{-1} is due to the carbonyl bond (C=O) stretching whereas peaks around 1030 cm^{-1} are t due to the stretch vibration of sulfoxide (S=O) group [48]. Small peaks between 650-910 cm^{-1} are due to C-H benzene ring vibrations [7, 49]. When SBS is added to bitumen (Figure-10(a)), two additional peaks appear at 966 cm^{-1} and 700 cm^{-1}, which are due to C=C bonds in butadiene segments and C-H bending in styrene segments, respectively [7, 50]. Similarly, a new

peak was observed at 1575 cm^{-1} in case of CR-modified bitumen which is characteristic of dienes present in CR (Figure-10(c)). Another peak was observed at 1540 cm^{-1} which Liu H. [51] et al. have attributed to frame vibration of benzene ring caused due to the addition of CR to base bitumen. Besides these, no additional appearance or disappearance of peaks was observed in case of polymer-modified bitumen. Hence, it can be said that the polymer-modification of bitumen is mainly physical in nature. These results are in alignment with those of Zhang et al. [33] who have also concluded that polymer-modification of bitumen is mainly a physical interaction. Airey stated that the modification of bitumen due to SBS results in physical crosslinking of the polymeric blocks into a three-dimensional network. In addition, Liu H. et al. [51] have also investigated the effect of CR on bitumen and have attributed physical interactions as the primary modification mechanism of bitumen. Abdelrahman et al. [52] have suggested swelling of CR particles by bitumen fractions as one of the prime mechanisms of modification using CR. In the FTIR spectrum of nanosilica powder, the major peak at around 1071 cm^{-1} is a typical characteristic of Si-O-Si linkages. However, when nanosilica is incorporated in bitumen along with polymers, the Si-O-Si peak shifts to higher wavelength of 1106 cm^{-1} (Figure-10(a)). This shift suggests that the siloxane bonds of nanosilica might interact with bitumen or probably bind with some of bitumen components which leads to a modified spectrum. In order to verify whether the shift arises due to silica structure or the surface groups of PDMS, we performed similar measurements using a) unmodified nanosilica which did not possess any PDMS surface groups and b) neat PDMS (without the silica). As shown in Figure-10 (d) the shift of the siloxane peak in the case of neat PDMS was negligible. However, the shift of siloxane peak of unmodified nanosilica was similar to what was obtained in case of PDMS-modified nanosilica. Hence, it can be concluded that it is the inner silica core structure that probably undergoes some chemical interactions with asphaltenes

and resins fractions of bitumen. This shifting of siloxane peak is consistent in all three systems. Lesueur [3] states that bitumen contains phenolic -OH groups and carboxylic acid groups and that chemical interactions with bitumen are not rare. Alhamali et al. [44] have suggested a formation of a new network structure between nanosilica and bitumen resulting from chemical and physical interactions that is temperature resistant and which anchors the polymer and bitumen together. Specifically describing this new network structure, investigations of Zhang et al. [33] who have modified bitumen using SBS and nanofillers like nano-ZnO and nano-TiO_2 have suggested a chemical reaction between asphalt and the hydroxyls of nano-ZnO and nano-TiO_2. Similarly, Yao et al. [34] have attributed the modification mechanism between nanosilica and bitumen to a chemical reaction between -OH groups of nanosilica and bitumen. Fini et al. [53] state that the oxygen atom in the hydroxyl groups present on the surface of nanosilica is highly electronegative and tends to form hydrogen bonds with polar aromatics and the asphaltene fraction of bitumen. In the present study, Aerosil®R202 is surface-modified with polydimethylsiloxane (PDMS) which is methyl terminated and hence such reactions are less likely. However, substantial silanol groups maybe present on the silica surface and PDMS might be adsorbed to the silica surface rather than being connected through covalent bonding (Litke, U.S. Patent No. 4,533,422) [54]. Hence, some chemical interactions between surface silanol groups or functional end groups of PDMS and polar aromatics and/or asphaltenes cannot be completely ruled out. Moreover, peaks that are characteristic of polymers are unaltered due to the addition of nanosilica, which means that the interactions between nanosilica and polymers are purely of physical nature. Due to the complexity of bitumen's chemistry and abundance of functional groups, it is difficult to pinpoint the exact chemical interactions between nanosilica and bitumen.

3.7. Dynamic Mechanical Analysis

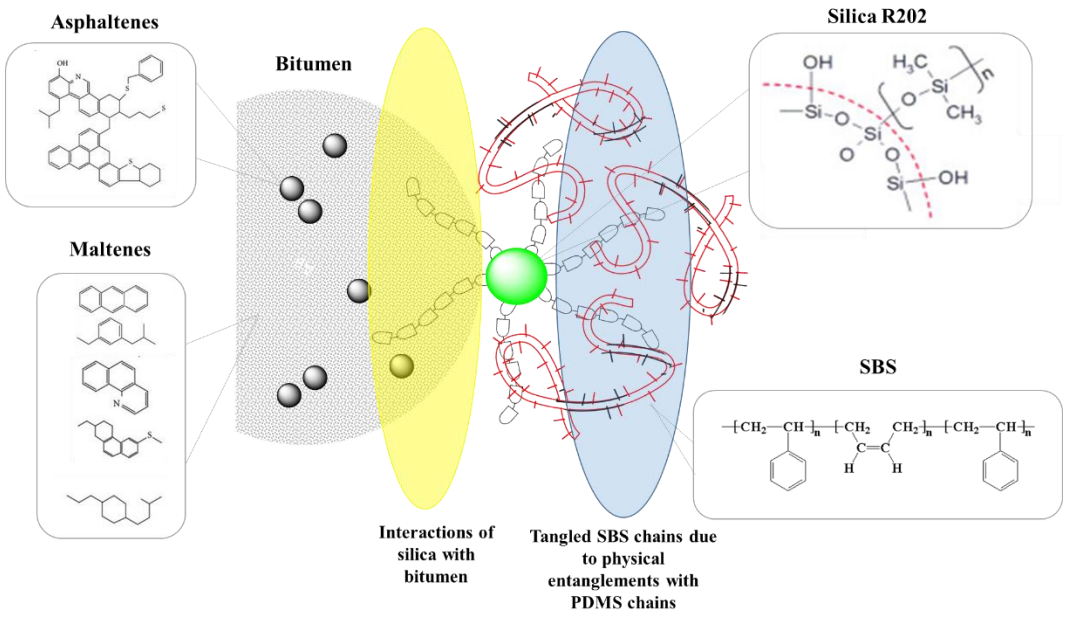


Figure-11: Schematic of polymer-matrix interactions and possible immobilization

Storage stability tests employed in this work reveal that nanosilica acts as compatibilizer between SBS and bitumen or CR and bitumen leading to a stable system under storage conditions. Compatibilization is established by interactions of nanosilica with bitumen through chemical interactions (as seen from the FTIR results discussed above) whereas the interactions between nanosilica and polymers, we believe, arise due to the PDMS chains in PDMS modified-nanosilica physically entangling with SBS and/or CR chains (Figure-11). The latter mechanism is illustrated in Figure-11, which shows the entanglements of SBS chains (red) with surface PDMS groups of nanosilica (grey). These entanglements cause immobilization of SBS or CR chains which leads to slower dynamics in the vicinity of nanofiller and, hence, to an increase in modulus while at the same time preventing a phase separation by anchoring polymers and bitumen together.

To further validate this theory, the interactions between the polymers used and nanosilica, in the absence of bitumen were investigated. Different concentrations of PDMS modified-

nanosilica in an SBS matrix were studied. SBS was chosen because of the ease of preparing SBS-silica composites using twin-screw micro-extruder, but the discussion and conclusions that follow can be extended to the system with CR and PDMS modified-nanosilica, since CR mainly consists of natural rubber, cis-butadiene rubber and/or styrene-butadiene rubber (SBR) [55].

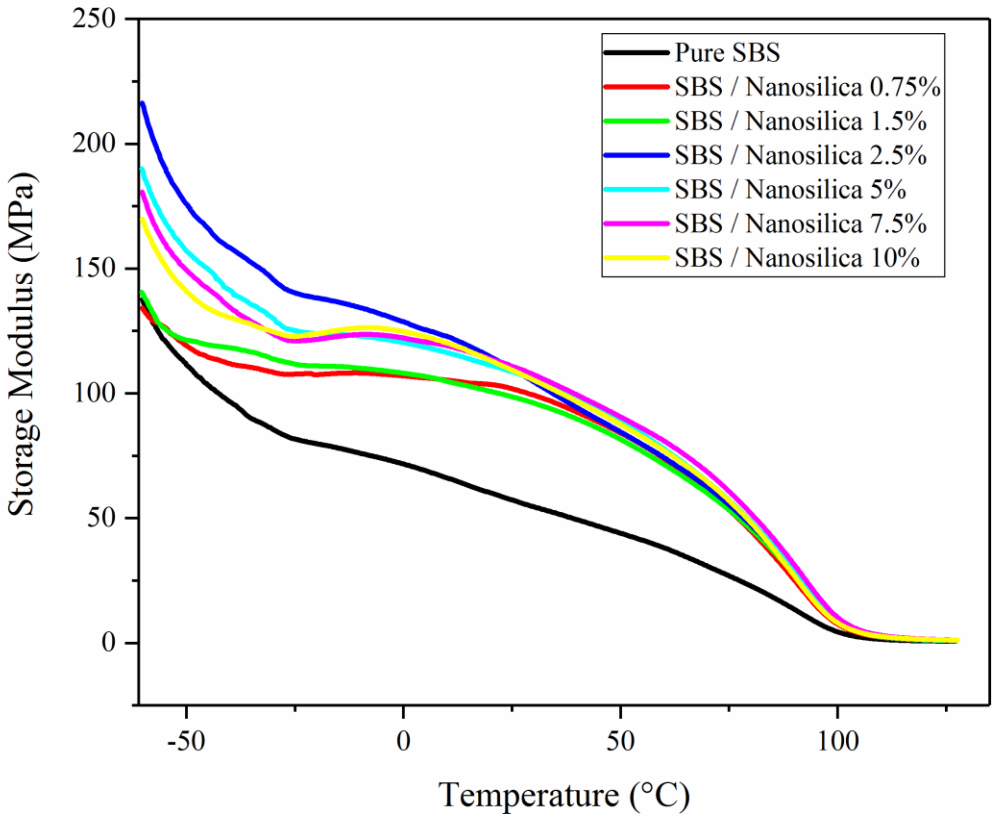


Figure-12: Dynamic mechanical properties of SBS/nanosilica composites

Storage modulus vs. Temperature

SBS samples containing nanosilica show an increase in the modulus as compared to pure SBS (Figure 12). This increase arises due to the higher degree of reinforcement of nanosilica in the SBS matrix. Chen et al. [56] have investigated poly (butylene succinate)/fumed silica

nanocomposites and have observed the increase in the modulus of the composite with increasing filler concentration. They have attributed this increase to formation of physical network structures that leads to immobilization of polymer chains and hence, causes enhanced polymer/filler compatibility. Besides silica, Liao et al. [57] have investigated the effect of montmorillonite (MMT) in polybutadiene rubber (PB) and found that the stronger interfacial interactions result in good dispersion of the nanoclay layers in PB, and the layered structure of MMT can function as "pseudo-crosslinking" points. These "pseudo-crosslinking" points can be correlated to the entanglements of surface polydimethylsiloxane siloxane (PDMS) groups with SBS matrix chains in the present case, which further results in a remarkable increased storage modulus of SBS composites containing nanosilica.

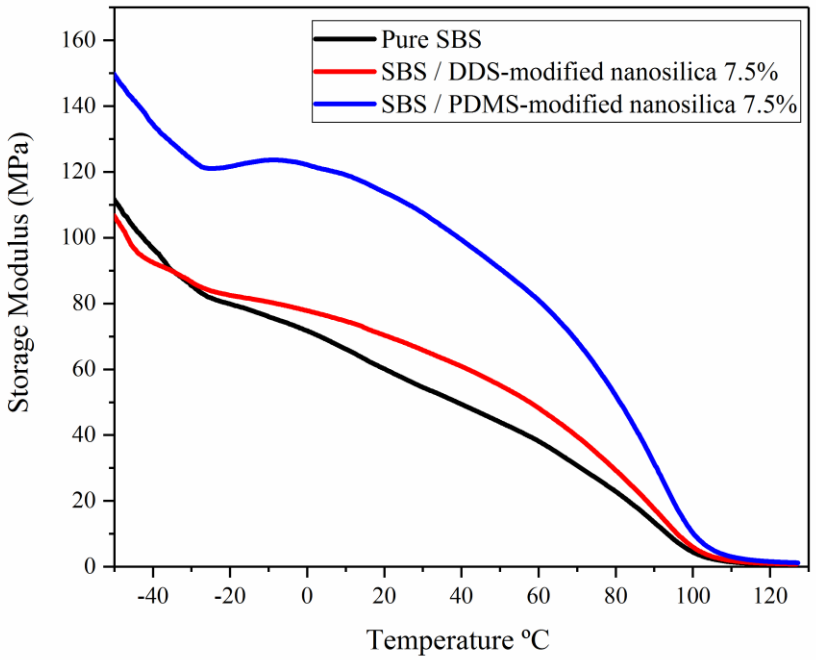


Figure-13: Effect of surface groups on dynamic mechanical properties of SBS/nanosilica composites: Storage modulus vs. Temperature

The above suggest that the increase in the moduli and the improvement of the final binders (including bitumen as well) are specifically due to the interaction of PDMS/nanosilica with the polymers. To further probe this question, an experiment was performed with another type of nanosilica that was surface-modified with dimethyldichlorosilane (DDS) instead of PDMS, but possessed almost identical properties with the PDMS modified silica. PDMS-modified nanosilica (Aerosil®R202) has a specific surface area (BET) of 80-120 m^2/g, average primary particle size of 14 nm, SiO_2 content of ≥ 99.8% and carbon content of 3.5-5%. On the other hand, DDS-modified nanosilica (Aerosil®R972) possessed comparable properties with a specific surface area (BET) of 90-130 m^2/g, average primary particle size of 16 nm and SiO_2 content of ≥ 99.8% but with much shorter (non-polymeric) surface groups and hence, a lesser carbon content of 0.5-1.2%. It was believed though that this difference in organic content and physical length of surface groups played a critical role to the final properties of polymer blends.

As seen from Figure-13, PDMS-modified nanosilica/SBS composite shows a prominent rubbery plateau, which is a characteristic of a crosslinked structure in classical rubbers or "pseudo-crosslinking" points in this case. On the other hand, DDS-modified nanosilica/SBS composite does not exhibit a prominent rubbery plateau. The above strengthens the argument that the occurrence of the rubbery plateau is due to physical entanglements between surface chains of PDMS-nanosilica and SBS matrix. In fact, it rather seems to be very close to the pure SBS polymer. In an analogous experiment, Mascia et al. [58] have investigated the role of amine silane surface functionalization of silica for silica/epoxy nanocomposites and have attributed these surface groups for an increase in the rubber plateau modulus for their system.

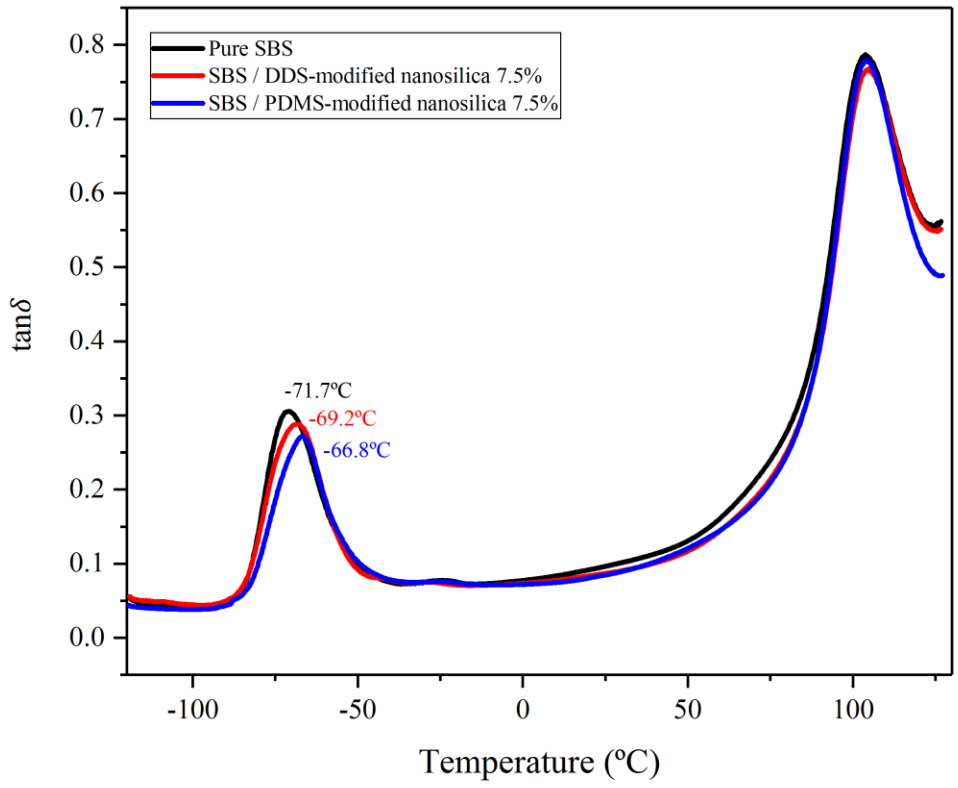


Figure-14: Effect of surface groups on dynamic mechanical properties: tanδ vs. Temperature

It can be seen from the plot of tanδ vs. temperature (Figure-14) that SBS/nanosilica composites show a drop in peak height as well as a slight shift in the glass-transition temperature, T_g, to higher temperatures as compared to that of pure SBS. The height of these peaks is a measure of the extent of mobility of the polymer chains. PDMS-modified nanosilica/SBS composite has a shorter peak height in comparison to that of DDS-modified nanosilica/SBS composite and hence, it has a much stronger effect in restricting the dynamics of SBS matrix chains due to entanglement effect of PDMS with SBS. This effect leads to an increase in the modulus. When compared to DDS-modified nanosilica/SBS composites, PDMS-modified nanosilica also shows a higher increase in T_g, which further explains the strong reinforcing effect [59]. No major shift in the T_g

of the polystyrene phase is observed. This is probably because of the lesser weight fraction of styrene blocks (30 wt. %) as opposed to much larger weight proportion of butadiene blocks (70 wt. %) and also due to the fact that styrene blocks are more rigid and cannot be influenced as easily as the flexible blocks of butadiene. Thepprati et al. [60] have investigated the effect of surface modification of silica on the dynamics of natural rubber (NR) vulcanizates. They observed that the addition of silica results in higher T_g of the composite material as well as that silane-modified silica/NR composite demonstrates a higher T_g than that of unmodified silica/NR composite. They attribute this increase in T_g to formation of a pseudo network, which leads to hindered movements of rubber matrix chains.

In order to calculate the activation energy needed to mobilize (or disentangle) these entanglements (Table-3) near the nanosilica surface, the following Arrhenius-type equation already used for the same purpose by Pourhossaini and Razzaghi-Kashani [59] was used

$$\frac{E}{E_0} = exp\left[-\frac{E_{act}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

where E and E_o are the storage moduli at temperatures T and T_o respectively. E_{act} is the activation energy while R is the universal gas constant.

Tsagaropoulos and Eisenberg [61] observed a secondary relaxation at a temperature of 60-100°C above the first peak of glass transition temperatures in tanδ for their silica-filled composites. They have attributed this relaxation to the movement of immobilized polymer chains due to the presence of silica. Hence, the temperatures of -50°C and 50°C were chosen as T_0 and T respectively to include this secondary transition and to exclude the contributions of main transitions of T_g of polystyrene and polybutadiene blocks (as seen from tanδ vs. temperature plot in Figure-14) while calculating this activation energy.

Nanosilica loading (wt. %)	Activation Energy (kJ/mol)
0.75%	2.1
1.50%	2.4
2.50%	4.4
5%	3.4
7.50%	3.0
10%	2.8

Table-3: Activation energy of mobilizing SBS / nanosilica entanglements

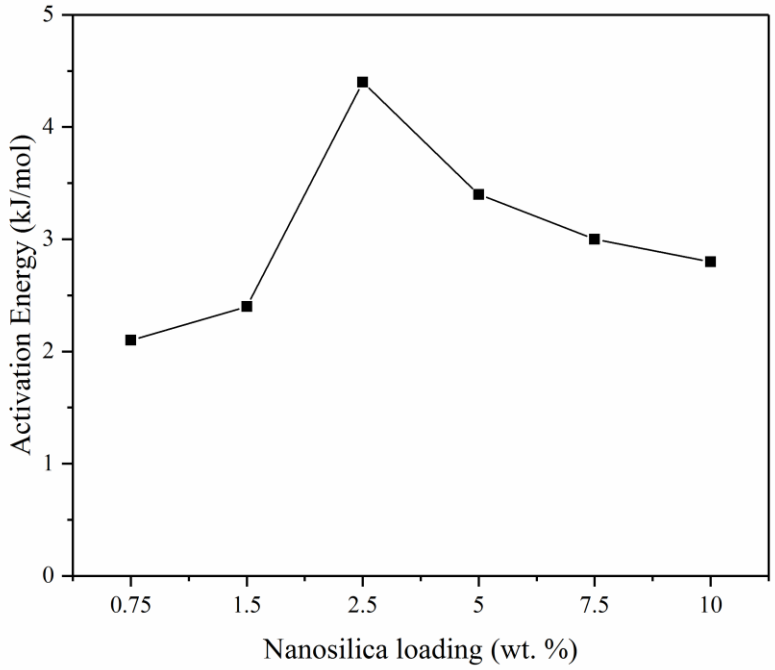


Figure-15: Effect of nanosilica loading on activation energy of disentanglements

In agreement with the findings of Pourhossaini and Razzaghi-Kashani [59], Figure-15 shows that as the nanosilica content is increased, the interfacial interactions are increased and

hence, a higher activation energy is needed to disentangle them. However, at much higher filler contents, nanosilica tends to aggregate and hence, the filler-filler interactions begin to dominate over polymer-filler interactions. Thus, a gradual drop in the activation energy was seen, as less energy is needed to mobilize these diminished entanglements due to aggregation of nanosilica. Rong et al. [62] have investigated the interfacial interactions between polypropylene and surface-modified nanosilica and have concluded that the interfacial interactions occur at very short ranges and hence, maximum interfacial interactions occur when the filler is used at lower concentrations.

Since this mechanism appears to take place with a variety of polymers and surface-grafted fillers including natural rubber [60] and styrene-butadiene rubber [63] is safe to extrapolated that it can be present between CR and PDMS-surface modified nanosilica as well.

4. CONCLUSIONS

A series of nanosilica and polymer modified bitumen composites were synthesized and characterized. Nanosilica helps in improving the rheological properties including complex modulus and rutting factor of pure bitumen, mechanical properties of bitumen/aggregate composites and resistance to thermal degradation. Nanosilica not only acts as a mechanical reinforcement but also serves as a compatibilizing agent between the polymers and bitumen. Moreover, CR can be used to replace SBS when used with nanosilica without any significant difference in performance of the binder. The rheological performance of the SBS/CR-nanosilica-modified binder is relatively weaker than the systems containing polymer modifiers of SBS and CR when used alone. Finally, in addition to evaluation of performance enhancements of the modified binders with respect to pure bitumen, a detailed investigation of the interfacial mechanisms between bitumen, polymers and nanosilica that are responsible for the modification of bitumen is presented. Polymer-modification of bitumen is a purely physical interaction whereas some chemical interactions between bitumen and nanosilica results upon the addition of nanosilica to bitumen.

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